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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
Crystalline, silvery films of the flexible, semiconducting polymer, "polyacetylene," $(CH)_x$, can be doped readily, either chemically or electrochemically, to give a series of either p-type or n-type semiconductors. As doping proceeds, their conductivity increases rapidly (over twelve orders of magnitude in certain cases). At a few mole percent dopant concentration, they undergo a semiconductor-metal transition and are converted to silvery-golden films of "organic metals." A qualitative summary of the most important experiments leading to the "soliton" concept of bonding in the semiconducting material will be pre-

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20. sented. This will stress, in particular, the change in Curie and Pauli magnetic susceptibilities of the $(CH)_x$ as it is doped p-type in a controlled, homogeneous fashion with AsF_5 or I_2 through the semiconducting to the metallic regime. Correlations between observed and calculated infrared spectra of doped $(CH)_x$ and $(CD)_x$ will also be described. Absorption and epr spectral data will be presented which will show that similar effects are observed when $(CH)_x$ is n-doped with a species such as sodium.

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Recent Advances in the Chemistry and Physics of
Polyacetylene: Solitons as a Means of Stabilizing
Carbonium Ions and Carbanions in Doped $(CH)_x$

by

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November 11, 1981

RECENT ADVANCES IN THE CHEMISTRY AND PHYSICS OF POLYACETYLENE: SOLITONS AS A
MEANS OF STABILIZING CARBONIUM IONS AND CARBANIONS IN DOPED $(CH)_x$

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of Matter, Department of Chemistry[+] and Department of Physics,[++] University of
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INTRODUCTION

There exists a new class of electronic materials formed as quasi-one-
dimensional organic polymers, which have the properties of semiconductors or
metals when suitably doped with donor or acceptor species. The prototype exam-
ple of these conducting polymers is polyacetylene, the simplest conjugated
polymer, which consists of parallel chains of CH groups as shown in Figure 1.[1]

Both the cis- and trans-forms (see Figure 1) can be prepared as silvery,
flexible films, which can be made either free-standing or on a variety of sub-
strates, such as glass or metal, with thicknesses varying from 10^{-5} to 0.5 cm.
The trans-isomer is the thermodynamically stable form; complete isomerization
from cis- to trans-$(CH)_x$ can be accomplished after synthesis by heating the
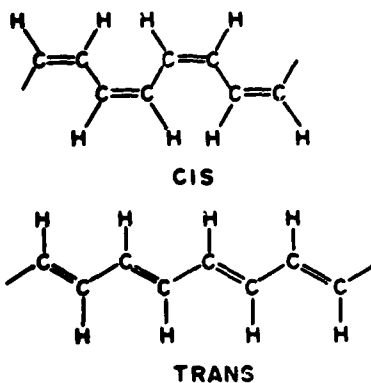film to temperatures above 150°C for a few minutes. Electron-microscopy

Figure 1. Cis and trans isomers of $(CH)_x$.

studies show that the as-formed $(CH)_x$ films consist of randomly oriented fibrils (typical fibril diameter ~200Å). The films can be stretch-oriented in excess of three times their original length with concomitant partial alignment of the fibrils. The bulk density is 0.4 g/cm^3, compared with 1.2 g/cm^3 as obtained by flotation techniques. Therefore, the polymer fibrils fill only about one third of the total volume and the effective surface area is quite high (~60 m^2/g). X-ray studies show that the $(CH)_x$ films are highly crystalline.

Recent studies have demonstrated that, after synthesis, $(CH)_x$ films can be chemically doped at room temperature with a variety of donors or acceptors to form n- or p-type semiconductors.[1] (See Table I) Doping to high levels (above ~1%) results in a semiconductor-metal transition giving a whole new class of metals with a wide range of electronegativity. Moreover, the existing experimental data already show that these materials have potential for use in a number of areas of future technology. Experimental studies at the University of Pennsylvania have demonstrated that doped polyacetylene might be useful in such diverse applications as: (1) the replacement of increasingly scarce conventional conductors by synthetic metals; (2) the development of lightweight, high-energy-density batteries; and (3) low-cost solar photovoltaic materials.

The electrical conductivity of polyacetylene can be varied in a controlled manner over thirteen orders of magnitude through chemical or electrochemical doping; results for three typical dopants are shown in Figure 2.[1] Values greater than 3 x 10^3 $\Omega^{-1}cm^{-1}$ have already been achieved with only partially aligned
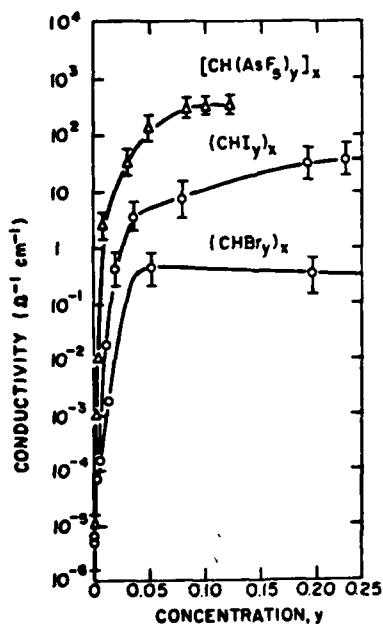

Figure 2. Electrical conductivity of doped trans-$(CH)_x$ film as a function of dopant concentration.

TABLE I

Examples of p- and n-Type Doping of $(CH)_x$

Selected Dopants for $(CH)_x$

p-Type Dopants	$(ohm^{-1}cm^{-1}$ at 25°C)
cis-$(CH)_x$	1.7×10^{-9}
trans-$(CH)_x$	4.4×10^{-5}
cis-$(CHI_{0.30})_x$	5.5×10^2
trans-$(CHI_{0.20})_x$	1.6×10^2
cis-$[CH(IBr)_{0.15}]_x$	4.0×10^2
cis-$[CH(AsF_5)_{0.10}]_x$	1.2×10^3
cis-$[CH(PF_6)_{0.033}]_x$	2.5×10^1
cis-$[CH(H^+AsF_6^-)_{0.1}]_x$	7×10^2
cis-$[CH(H_3O^+ClO_4^-)_{0.127}]_x$	1.2×10^3
cis-$[CH(ClO_4)_{0.065}]_x$	9.7×10^2
cis-$[CH(H_3O^+HSO_4^-)_{0.106}]_x$	1.2×10^3
n-Type Dopants	
cis-$[Li_{0.30}(CH)]_x$	2.0×10^2
cis-$[Na_{0.21}(CH)]_x$	2.5×10^1
cis-$[K_{0.16}(CH)]_x$	5.0×10^1
trans-$[Na_{0.28}(CH)]_x$	8.0×10^1
cis-$[(^nBu_4N)_{0.03}(CH)]_x$	1.0

Cis or trans refers to the principal isomeric species before doping.

samples, and analysis of the transport (electrical conductivity and related properties) and optical data implies that a further increase of at least one order of magnitude should be possible.

In simple terms, one may regard the bonding in $(CH)_x$ as being derived from the linking together of sp^2 hybridized (CH) units, the fourth carbon valence electron being in a p_π orbital perpendicular to the plane of the $(CH)_x$ molecule. A diagrammatic representation of the energy levels (band diagram) associated with the overlapping molecular orbitals of pi symmetry formed by joining (CH) units together is given in Figure 3. The species depicted range from $(CH)_2$, i.e., $H_2C=CH_2$, to $(CH)_x$. The filled π molecular orbitals correspond to the valence band, the empty π^* orbitals to the conduction band, and the $\pi \rightarrow \pi^*$ transition energy to the band gap in a semiconductor or insulator. If all the C-C bonds were of equal length, having a bond order of 1.5 (one σ bond and half-filled π bond), $(CH)_x$ would be a metal with zero band gap; if the band gap were large, the resulting material would be an insulator. In the case of trans-$(CH)_x$, where the C-C bond length alternation is small, a band gap of approximately 1.5 eV results; the pure material is therefore a semiconductor.[1]

The carriers (electrons and/or [positive] holes) generated by the doping of $(CH)_x$ result from charge transfer. Charge transfer occurs from polymer to acceptor (A) with the polymer chain acting as a poly(cation) in the presence of an A^- species. For a donor (M), the polymer chain acts as a poly(anion) in the presence of M^+ species. The A^- or M^+ ions reside between polymer chains. Reversible doping can be carried out electrochemically,[2] and chemical compensation has been demonstrated. For example, after doping and subsequent chemical compensation, the optical absorption spectrum converts back to that of the undoped polymer.[3] Therefore, since the anisotropic optical properties of the undoped polymers are characteristic of the quasi-one-dimensional $(CH)_x$ chains,
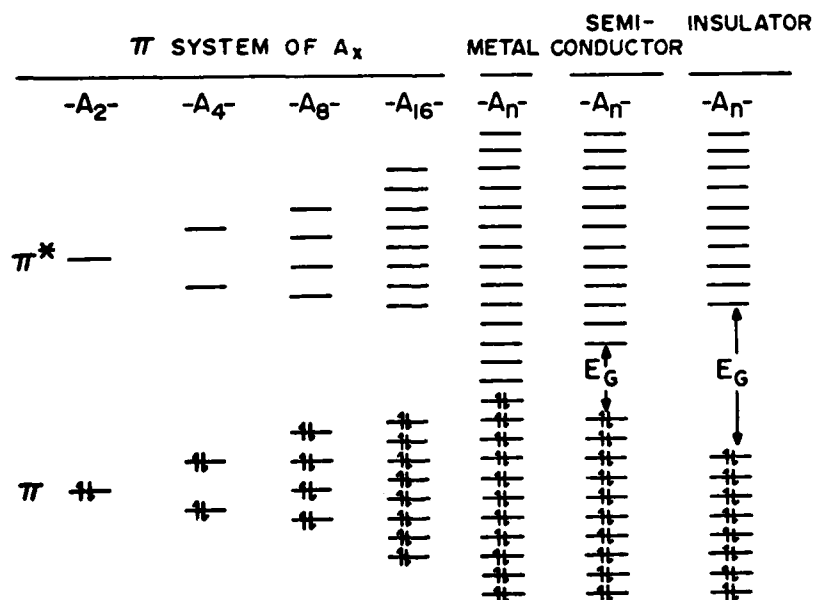

Figure 3. Diagrammatic representation of the energy levels (band diagram) associated with the overlapping of molecular orbitals of π symmetry formed by joining (CH) units together.

the reversibility implies that the $(CH)_x$ chains remain intact in the doped polymer.

In trans-$(CH)_x$, three main electronic regimes are observed: (1) the semi-conducting regime where the dopant concentration is small (<0.1%) and the properties are similar to those of a doped semiconductor; (2) the metallic regime where the dopant concentration is >~6% and the electronic properties (i.e., conductivity, thermoelectric power, absorption and reflectance spectra, specific heat, magnetic susceptibility, etc.) are characteristic of a metal;[1] and (3) the transitional region where the properties are intermediate between those of the semiconducting and metallic limits.[4] This intermediate regime is in many ways the most interesting; for example, although the electrical conductivity is high, there appears to be no Pauli susceptibility suggesting the possibility of a non-traditional transport mechanism.[4] However, since this transitional regime is not well understood, the present discussion will be limited primarily to the semiconducting regime and to the soliton concepts which are relevant to dilute doping.

SEMICONDUCTING REGIME: SOLITONS IN POLYACETYLENE

If the bond lengths in pure trans-$(CH)_x$ were uniform, the polymer would be a quasi-one-dimensional metal with a half-filled band. Such a system is unstable with respect to a dimerization distortion (the Peierls instability) in which adjacent CH groups move towards each other, forming alternately short (or double) bonds and long (or single) bonds, thereby lowering the energy of the system and opening the semiconductor band gap. Clearly, by symmetry, one could interchange the double and single bonds without changing the energy. Thus, there are two lowest-energy states, A and B, having two distinct bonding structures as shown in Figure 4. This twofold degeneracy leads to the existence of nonlinear topological excitations, bond-alternation domain walls or solitons, which appear to be responsible for many of the remarkable properties of $(CH)_x$.

When a single chain of cis-$(CH)_x$ begins to isomerize, the isomerization process can, in principal, commence at different parts of the chain, one having configuration (A), the other, configuration (B). When these two different configurations meet, a free radical is produced as shown schematically in Figure 4.
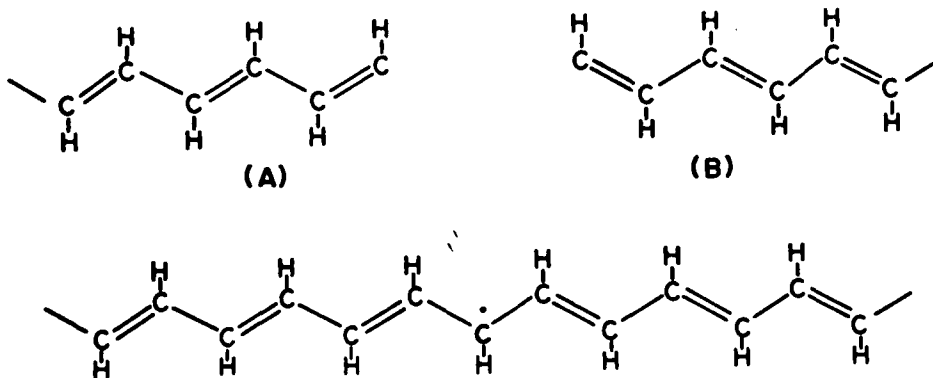

(A)   (B)

Figure 4. Formation of a neutral soliton by joining together the two lowest energy states, (A) and (B) of trans-$(CH)_x$.

This has been confirmed experimentally - when pure $\underline{cis}$-(CH)$_x$, possessing no free spins, undergoes isomerization, approximately one in 3000 of the (CH) units in the resulting $\underline{trans}$-(CH)$_x$ is in the form shown in Figure 4 with an unpaired spin and a Curie law magnetic susceptibility. This species is actually a valid excited state of $\underline{trans}$-(CH)$_x$, which could be formed in principal, for example, if $\underline{trans}$-(CH)$_x$ could be heated to a sufficiently high temperature without out thermal decomposition. It would be expected that this free spin could be readily ionized leaving behind a positive charge. This has indeed been observed. Thus if (CH)$_x$ is carefully and slowly oxidized by, for example, AsF$_5$, a stabilized carbonium ion is formed; the Curie spins originally present decrease almost to zero, and the conductivity of the material increases greatly.

If, for simplicity, it is first assumed that the unpaired spin resides completely on one (CH) unit, it may be regarded as being located in a non-bonding π molecular orbital, since it is not formally involved in π bonding to either of the adjacent (CH) units. Since a non-bonding π molecular orbital will lie midway between the π and π^* molecular orbitals, it is apparent that the energy level giving rise to this free spin will fall in the center of the band gap as shown in Figure 5. This localized non-bonding state formed at the boundary between the two degenerate phases (A and B) has been termed a "neutral soliton." Analogously, when this electron is removed, as described earlier, to give a carbonium ion, a mid-gap "positive soliton" is produced, as shown in Figure 6. Alternatively, if an electron is added to a neutral soliton as, for example, in the $\underline{n}$-doping of (CH)$_x$ by sodium to produce a stabilized carbanion, the mid-gap state is doubly occupied and a "negative soliton" is generated as depicted in Figure 7.

The presence of neutral solitons induced as defects during isomerization is a fortunate accident, for the number of thermally induced neutral soliton excitations in undoped (CH)$_x$ would be far too small to be observable. In this context, however, it must be stressed that it is not necessary to first have neutral solitons in order to obtain positive (or negative) solitons. For example, it has been shown experimentally[4] that on careful $\underline{p}$-doping of (CH)$_x$ with AsF$_5$
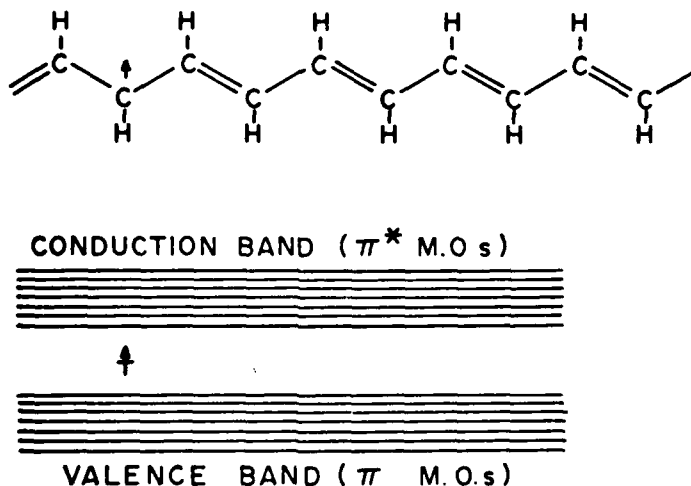

CONDUCTION BAND (π^* M.O s)

VALENCE BAND (π M.O.s)

Figure 5. Diagrammatic representation of a neutral soliton (free radical located on a non-bonding π molecular orbital) in $\underline{trans}$-(CH)$_x$.
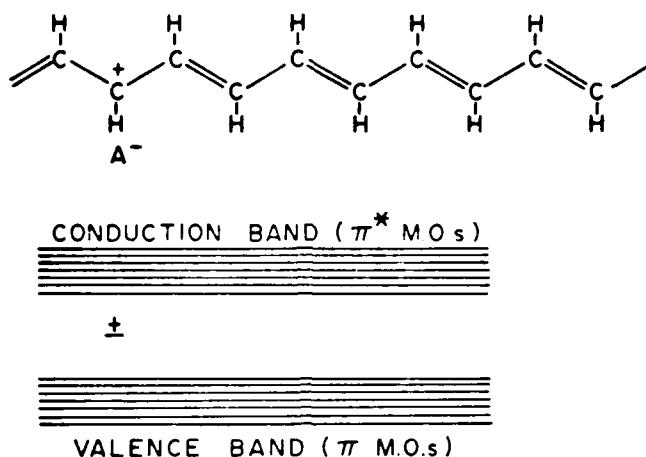
Figure 6. Diagrammatic representation of a positive soliton (carbonium ion located on a non-bonding π molecular orbital) in <u>trans</u>-$(CH)_x$.
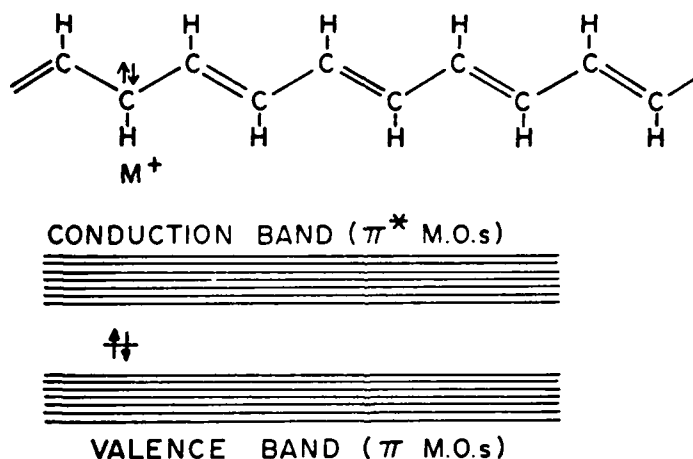

Figure 7. Diagrammatic representation of a negative soliton (carbanion located on a non-bonding π molecular orbital) in <u>trans</u>-$(CH)_x$.

that: (i) the original free Curie spins in $(CH)_x$ decrease as indicated above and (ii) even though the amount of dopant species is far in excess of that necessary to remove the original free spins, no additional Curie spins appear. This is consistent with the generation of charged solitons according to the doping model shown in Figure 8.

In the previous discussion, it has been assumed that a soliton has been localized on a single (CH) unit. Detailed calculations have shown that minimization of the total energy spreads the soliton over a region of about 15 (CH) units.[5] Thus, for example, in the case of a positive soliton, although the
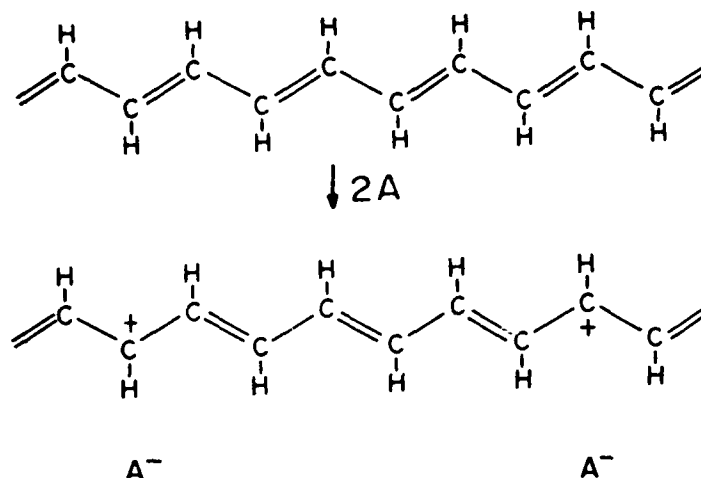
Figure 8. Diagrammatic representation of p-type doping of trans-$(CH)_x$ with no production of Curie or Pauli spins.

maximum charge density is adjacent to the counter anion, A^-, ~85% of the charge is spread out symmetrically on either side over ~15 (CH) units. This is qualitatively understandable, since it is recognized from symmetry considerations that the positive soliton formally located on a single (CH) unit will actually have some interaction with the p_π orbitals on the adjacent (CH) units. This delocalizes the non-bonding mid-gap state over many bond-lengths as shown schematically in Figure 9(b). It is apparent that considerable bond length distortion will be involved near the center of the soliton, since these bonds alone are responsible for adjusting the bond lengths of segment (A) with those of segment (B) (Figure 9(a)) in which the relative positions of the formally single and double bonds are reversed. Since the energy to distort a bond is proportional to the square of the distortion, it is apparent that if the distortion were spread out over several bonds, the distortional energy required would be less. Hence, the system is stabilized if the bond distortion is taken up by several bonds as shown diagrammatically in Figure 9(b) to produce a positive soliton or domain wall, which separates (A) type domains from (B) type domains. We note that within these domain walls (particularly near the center), the C-C bond lengths tend to become very nearly equal. It might at first be thought that the greatest stabilization would result if the distortion were spread out over the whole chain. This, however, is not the case because of the Peierls distortion stabilizing energy, which, for a hypothetical 1-dimensional molecule, predicts that a single-double bond alternating structure has a lower total energy and thus, is more stable than one consisting totally of equal (bond order 1.5) linkages. These two opposing distortional effects involving bond lengths result in the soliton domain walls in $(CH)_x$ being extended to approximately 15 (CH) units.
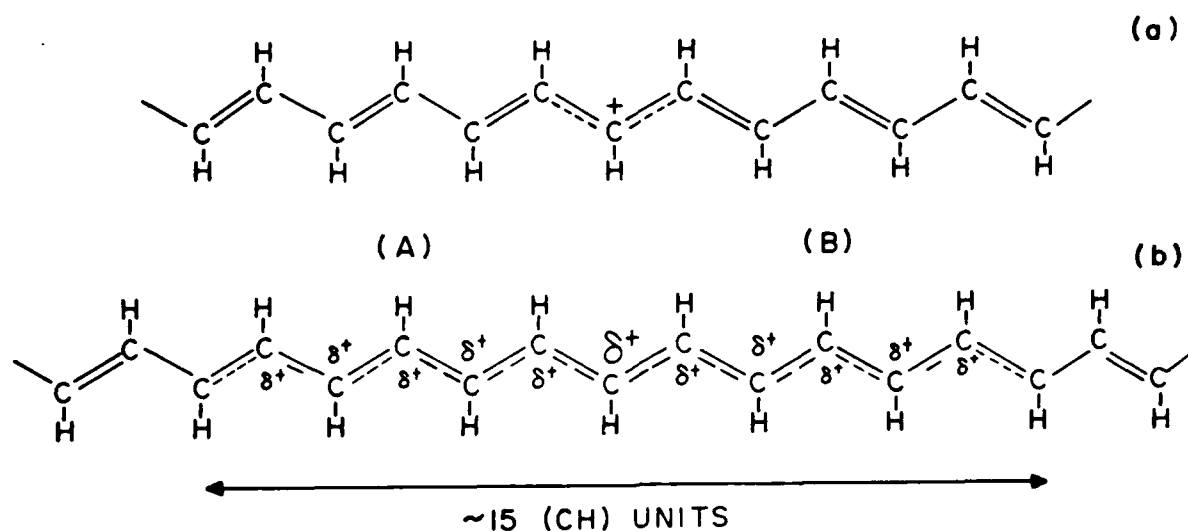
Figure 9. Diagrammatic representation of the delocalization of a positive soliton in trans-$(CH)_x$: (a) charge localized on one (CH) unit; (b) charge localized over ~15 (CH) units.

Conductivity-temperature studies show that the conduction process in $(CH)_x$ in the semiconducting regime proceeds by a hopping mechanism.[6] Although this may involve movement of a positive or negative soliton along a chain, recent calculations predict that an interchain hopping mechanism involving the "capture" of a mobile electron from a neutral soliton in one chain by a relatively non-mobile positive (or negative) solition in an adjacent chain may be the dominant mechanism. The experimental results for undoped trans-$(CH)_x$ are in excellent agreement with this inter-soliton hopping theory.

Implicit to the whole concept of soliton doping in $(CH)_x$ in the semiconducting regime is that as doping proceeds, there is no increase in the number of free spins (neutral solitons). This is consistent with measurements on carefully doped $(CH)_x$.[4] In this respect, the behavior of $(CH)_x$ is exactly the opposite of that found during the doping of a classical semiconductor such as silicon, in which the number of unpaired spins increases as doping proceeds. This phenomenon in $(CH)_x$ is due to the unique symmetry of the material in the trans form

as shown in Figure 10. Thus if a perfect (diamagnetic) trans-$(CH)_x$ sequence were treated with two p-type dopant species, A, and two electrons were removed from two different filled π orbitals, then two unpaired electrons would be found (associated with two positive holes in the valence band), provided no change in the direction of bond alternation had occurred. However, as noted above, the production of unpaired electrons is not observed experimentally. If, however, a rearrangement of electrons occurs as shown in Figure 10 with a concomitant rearrangement of formally single and double C-C bonds, the positive holes will rise out of the valence band as shown. Since (A) and (B) segments of $(CH)_x$ are energetically identical and since the "rising" of positive holes results in stabilization of a system,* the formation of mid-gap positive solitons is favored energetically as compared to positive holes in the valence band. As noted previously, the positive charge is not localized on just one (CH) unit as shown in Figures 9 and 10 but is actually spread over approximately 15 (CH) units, the magnitude of the charge on each (CH) unit diminishing with increasing distance from the counter anion, A^-, adjacent to the chain. Thus, the observation that the Curie susceptibility of trans-$(CH)_x$ decreases on careful p-doping due to the conversion of neutral solitons to positive solitons and that additional positive solitons are formed with no production of Curie spins is consistent with the soliton concept of doping.

Spectroscopic evidence for the mid-gap soliton state is obtained from the change in the absorption spectrum of trans-$(CH)_x$ as a result of doping. The intensity of the band gap transition at approximately 1.5 eV decreases as a new transition, turning on at approximately 0.75 eV, appears and increases in intensity during doping.[7] Further strong evidence for the formation of solitons during p-doping is obtained from the infrared spectra of both trans-$(CH)_x$ and trans-$(CD)_x$ doped to the semiconducting regime.[8] The soliton infrared active vibrational modes in $(CH)_x$ appear at 1385 cm^{-1} and 900 cm^{-1}; the corresponding modes in the deuterated material occur at 800 cm^{-1} and 1100 cm^{-1}, respectively. These modes are predicted both for $(CH)_x$ and $(CD)_x$ within a few percent accuracy by calculations based on the soliton theory.

CONCLUSION

In conclusion, experimental and theoretical evidence obtained to date is consistent with the soliton concept of bonding in parent $(CH)_x$ and $(CH)_x$ doped within the semiconducting regime. The solitons in trans-$(CH)_x$ are proving to be fascinating to both chemists and physicists. To the physicists, they represent non-linear topological excitations resulting from the fundamental broken symmetry of the trans-$(CH)_x$ chain. As a result, the study of polyacetylene is leading to a deeper understanding of such esoteric concepts as fractional charge and particle confinement. To the chemists, solitons represents a fundamental mechanism for stabilization of the carbonium ion and the carbanion. In effect, the switch in bond alternation and the associated distortions provide a kind of "solvation" energy which acts to stabilize and delocalize the added charge on the chain. In this sense, the existence of solitons is fundamentally responsible

*Electrons may be regarded as analogous to billiard balls - a system is stabilized by their rolling downhill! Positive holes may be regarded as analogous to balloons - a system is stabilized by their floating upwards!
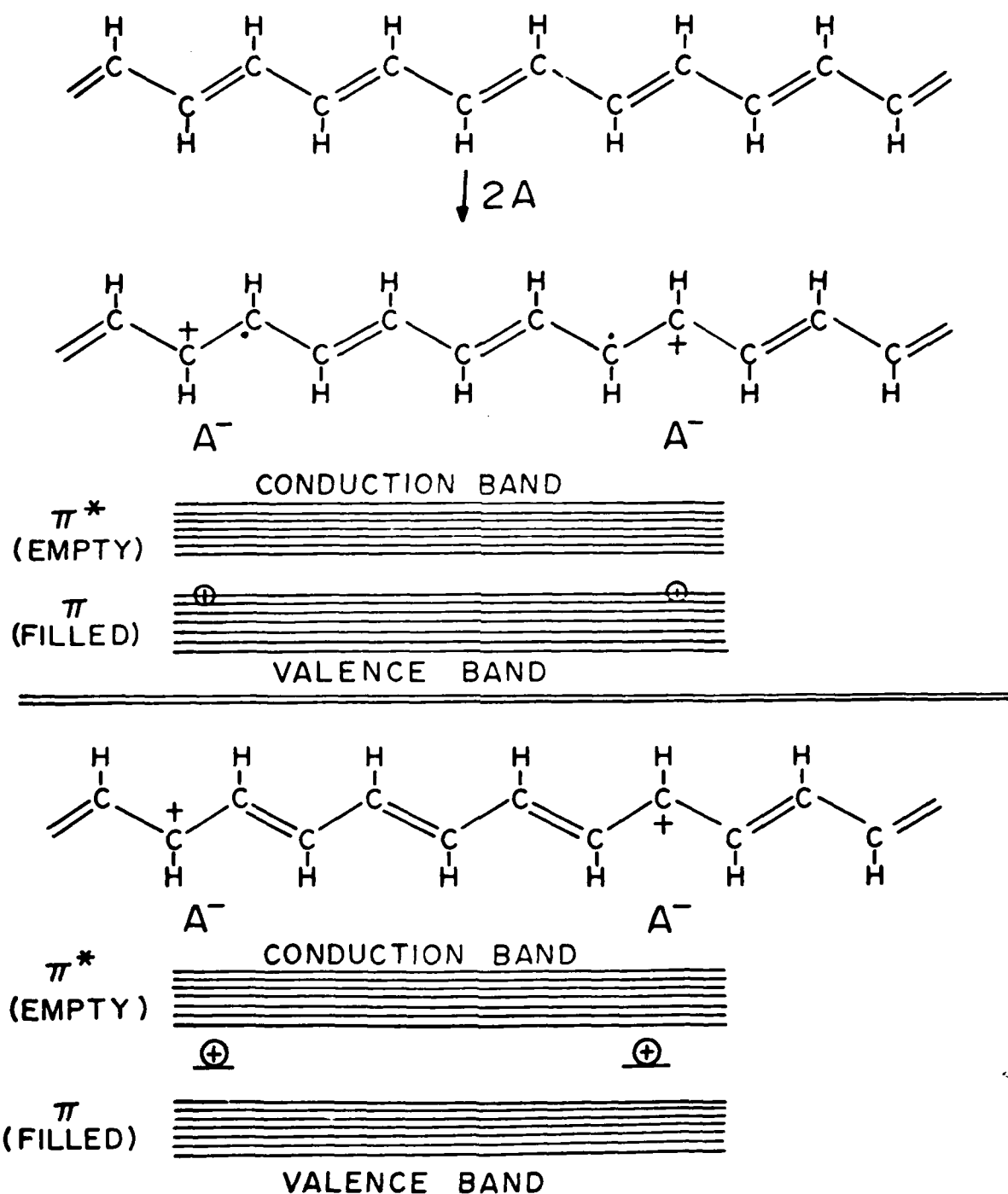
Figure 10. Diagrammatic representation of the formation of a positive soliton on p-doping trans-(CH)$_x$.

for the ease with which polyacetylene can be doped, n-type or p-type, through charge transfer.

Although results of detailed calculations have been presented to describe the transition from isolated solitons at low dopant concentrations to the metallic state at high dopant concentration, much remains to be done. Heavily doped $(CH)_x$ exhibits the electronic properties of a true metal. Above ~6% doping, $(CH)_x$ displays high conductivity,[6] a Pauli temperature independent paramagnetic susceptibility,[4] a linear dependence on temperature of the thermopower[9] and low temperature heat capacity,[10] the infrared properties of a metal,[1] etc. There is strong evidence leading to the conclusion that in this metallic regime, the C-C bond lengths have become equal since (for both p- and n-doped $(CH)_x$) the band gap $(\pi-\pi^x)$ transition disappears.[3] At this degree of doping, the solitons may be regarded as having overlapped with each other to form a conduction band which fills in the semiconductor band gap. On heavy doping, $(CH)_x$ becomes a metal, not a degenerate semiconductor, as does a classical semiconductor such as Si, in which the band gap remains even after it is heavily doped to concentrations well above the semiconductor-metal transition. In a general sense, the implied change from bond-alternating to nearly uniform bond structure is consistent with the soliton doping mechanism. However, a detailed understanding of the transition to metallic behavior is lacking. The intermediate transition regime remains as the least well understood aspect of the problem and presents an exciting challenge for continued study.

ACKNOWLEDGMENT

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